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<p>(21) International Application Number: PCT/EP98/07219 (22) International Filing Date: 4 November 1998 (04.11.98) (30) Priority Data: 97203628.9 21 November 1997 (21.11.97) EP (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): HOGT, Andreas, Herman [NL/NL]; Deurningerstraat 58, NL-7514 BJ Enschede (NL). FISCHER, Bart [NL/NL]; Bitterschoten 42, NL-3831 PC Leusden (NL). SPIJKERMAN, Geesje, Klasina [NL/NL]; Lijsterbeslaan 18, NL-7421 AS Deventer (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: EXTRUSION PROCESS FOR ENHANCING THE MELT STRENGTH OF POLYPROPYLENE</p> <p>(57) Abstract</p> <p>The invention relates to a process for enhancing the melt strength of polypropylene comprising the steps of: mixing the polypropylene with at least one peroxydicarbonate; reacting said polypropylene and peroxydicarbonate at a temperature between 150 °C and 300 °C, with the proviso that the peroxydicarbonate is not in the form of an aqueous dispersion.</p>		

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EXTRUSION PROCESS FOR ENHANCING THE MELT STRENGTH OF POLYPROPYLENE

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The invention pertains to a process for enhancing the melt strength of a polypropylene by mixing a peroxydicarbonate with the polypropylene and heating the polypropylene/peroxydicarbonate mixture.

10

Such a process is known from EP-B-0 384 431. This reference describes a process for preparing polypropylene (PP) with a branching index of less than 1 comprising (1) mixing a low decomposition temperature peroxide, such as a peroxydicarbonate, with the PP, (2) heating or maintaining the resulting mixture at a temperature from room temperature up to 120°C, and then (3) heating the PP at a temperature of 130 to 150°C to deactivate substantially all the free radicals present in said PP. The obtained PP has a significant amount of long chain branches and has an increased weight average molecular weight giving the polymer a significant strain hardening elongational viscosity. It is mentioned that in step (3) the heating may be done by extrusion or in a fluidized bed. It is further stated that at a temperature above 120°C an essentially linear polymer with little or no branching is obtained.

15

Apparently, the significant strain hardening elongational viscosity is related to an improved melt strength of the obtained PP due to long chain branching. It is only mentioned in this publication that step (3) of this process can be performed by extrusion, in the examples the entire process is carried out in a sealed reaction vessel. A disadvantage of this process is that it comprises three steps, which is undesirable in practice.

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DE-A-4340194 (US 5,416,169) describes a process for preparing PP having a high melt strength and a chain branching coefficient of 1, by mixing bis(2-ethylhexyl)peroxydicarbonate with a linear, crystalline PP, followed by heating

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at 70 to 150°C. In a subsequent step, the PP is taken out of the reaction vessel and is melt-kneaded. The peroxydicarbonate may be dissolved in an inert solvent before it is added to the PP. It is stated that other peroxydicarbonates, having a similar decomposition temperature, cannot be
5 used for this purpose.

A disadvantage of this process is that it can only be performed using one specific peroxide, i.e., bis(2-ethylhexyl)peroxydicarbonate. Another drawback is that the process is performed in two steps, which is undesirable and
10 uneconomical in practice.

It is the object of the present invention to provide a process which does not have the above-mentioned drawbacks and which process yields PP having a good melt strength.
15

To this end, the present invention provides a process for enhancing the melt strength of polypropylene comprising the steps of:

- mixing the polypropylene with at least one peroxydicarbonate;
- reacting said polypropylene and peroxydicarbonate at a
20 temperature between 150°C and 300°C, with the proviso that the peroxydicarbonate is not in the form of an aqueous dispersion in a polar medium with at least 90% by weight of the initiator particles being smaller than 50µm and at least 99% by weight of the initiator particles being smaller than 65µm. Preferably, the reaction conditions are chosen such that more
25 than 50% by weight, more preferably more than 70% by weight, and most preferably, more than 80 % by weight of the peroxide is still present when the mixture of peroxide and polymer reaches a temperature of 120°C, more preferably 150°C.

30 In the non-prepublished patent application now published as WO 97/49759 a process for enhancing the melt strength of a polypropylene is described,

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wherein a dispersion of an initiator, such as a peroxydicarbonate, in a polar medium, e.g., water, and with a particular particle size distribution, is contacted with the polypropylene and the resulting mixture is heated. This process may be carried out using an extruder.

5

The process according to the present invention is a process providing PP having an enhanced melt strength. Since the processing of PP frequently involves extrusion of the PP, either for pelletization in case of storage and transport or for further processing, i.e., the formation of an end product, it is a further advantage that the invention process is an extrusion process, allowing the modification of the PP, to enhance the melt strength, to be combined with said processing step.

The term "polypropylene" ("PP") refers to polymers or mixtures of polymers containing at least 50% by weight of polymerized propylene. Polymerization catalysts may be Ziegler-Natta, metallocene or other types giving stereospecific polymerization of propylene. Use may be made in this connection of homopolymers of propylene; random, alternating, or block copolymers; or random, alternating, or block terpolymers of propylene and another olefin. Generally, a propylene copolymer or terpolymer will contain one or more other olefins, such as ethylene, butene, pentene, hexene, heptene, or octene, but it may also comprise other olefinically unsaturated monomers or combinations of these, such as acrylates, styrene, styrene derivatives, acrylonitrile, vinyl acetate, vinylidene chloride, and vinyl chloride. It is preferred here to restrict the content of olefins other than propylene to 30% by weight of the copolymer. Especially suited to be used are homopolymers of propylene, copolymers of propylene and ethylene or mixtures of polypropylene and polyethylene containing not more than 10% by weight of polymerized ethylene.

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The melting point of normally solid commercially available PP is about 160-

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170°C. The melting point of propylene copolymers and tercopolymers in general can be lower. The process of the invention preferably is carried out at a temperature in the range of from 150 to 300°C, more preferably from 160 to 250°C, and most preferably from 170 to 225°C.

5

The molecular weight of the PP used can be selected from a wide range. Indicative of the molecular weight is the melt flow index (MFI). Use may be made of a PP having a MFI from 0.1 to 1000 g/10min (230°C, 21.6 N). Preferably, use is made of a PP having a MFI from 0.5 to 250 g/10min.

10

The process according to the present invention is suitably carried out in melt mixing equipment known to a person skilled in the art. Preferably, an extruder or a kneader is used. More preferably, use is made of a single or twin screw extruder. An internal mixer such as a Banbury mixer optionally coupled to an extruder may also be used.

15

The peroxydicarbonate may be mixed first with the PP and then the mixture may be extruded. Alternatively, the peroxydicarbonate may be added to the extruder already containing the PP by injection or spraying, or may be added together with the PP. It is preferred to introduce a solid peroxydicarbonate together with the PP into the extruder, for example, by using a feeder. The temperature setting of the extruder should allow the PP to melt, i.e. above 150°C. The screw speed typically is from about 25 to 500 rpm.

20

Normal residence time in the extruder is 15 sec. - 30 min. The longer residence times can be achieved by using additional static mixers etc.

25

The extruded strand may be further processed as known to one of ordinary skill in the art. Normally, the extruded strand is fed through a water bath and granulated using a granulator. Alternatively, the extruded modified PP is formed directly into a desired end product.

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It is preferred to carry out the process of the present invention in an atmosphere of an inert gas, such as nitrogen or argon. Preferably, nitrogen is used.

5

Solid as well as liquid peroxydicarbonates may be used in the process according to the present invention. A solution of a peroxydicarbonate in an inert solvent, such as isododecane, or in the form of frozen flakes, may also be used. Suitable inert solvents are known to one skilled in the art. It is preferred to use a solid peroxydicarbonate, in the form of, for example, flakes, finely divided particles (powder), or a liquid peroxydicarbonate, optionally adsorbed on or absorbed in a suitable carrier, such as silica or polypropylene powder or pellets. The use of a solid peroxydicarbonate permits a higher storage and processing temperature. Such higher temperature is beneficial when the peroxydicarbonate is to be introduced into an extruder using (loss-in-weight) feeders.

20

The peroxydicarbonates used in the process of the present invention have a half life of one hour at temperatures around 65°C.

Suitable examples of peroxydicarbonates have the formula the formula $R^1-OC(O)OOC(O)O-R^2$, wherein R^1 and R^2 are independently selected from the group consisting of CH_3 , 2- $i-C_3H_7O-C_6H_4$, $C_2H_5CH(CH_3)$, 4- $CH_3-C_6H_4$, $Cl_3CC(CH_3)_2$, C_7H_{15} , $c-C_6H_{11}CH_2$, 3- $t-C_4H_9-C_6H_5$, $Cl_3Si(CH_2)_3$, C_6H_5 , $CH_3CH(OCH_3)CH_2CH_2$, $C_6H_5OCH_2CH_2$, $C_6H_5CH_2$, Z- $C_8H_{17}CH=CH(CH_2)_8$, 2- $CH_3-C_6H_4$, $(CH_3)_2CHCH_2CH(CH_3)$, 3,4-di- $CH_3-C_6H_3$, Cl_3C , $CHCH(Cl)$, $ClCH_2$, $[C_2H_5OC(O)]_2CH(CH_3)$, 3,5-di- $CH_3-C_6H_3$, C_8H_{17} , C_2H_5 , $C_{18}H_{37}$, 2-oxo-1,3-dioxolan-4- CH_2 , $C_2H_5CH(Cl)CH_2$, 4- $CH_3O-C_6H_4$, $i-C_4H_9$, $CH_3SO_2CH_2CH_2$, $C_{12}H_{25}$, $C_6H_5CH(Cl)CH_2$, $H_2C=CHC(O)OCH_2CH_2$, 4- $NO_2-C_6H_4$, C_4H_9 , $C_{10}H_{21}$, $C_4H_9CH(C_2H_5)CH_2$, $H_2C=CHCH_2$, 2- $Cl-c-C_6H_{10}$, $H_2C=C(CH_3)CH_2$, $c-C_6H_{11}$, $ClCH_2CH_2$, 4- $[C_6H_5-N=N]-C_6H_4CH_2$, $C_{18}H_{33}$, 1-naphtyl, 4- $t-C_4H_9-C_6H_{10}$, 2,4,5-tri-

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Cl-C₆H₂, Cl(CH₂)₃, C₁₄H₂₉, 9-fluorenyl, 4-NO₂-C₆H₄CH₂, 2-i-C₃H₇-C₆H₄,
CH₃OCH₂CH₂, H₂C=C(CH₃), 3-CH₃-C₆H₄, BrCH₂CH₂, 3-CH₃-5-i-C₃H₇-C₆H₃,
Br₃CCH₂, C₂H₅OCH₂CH₂, 4-CH₃OC(O)-C₆H₄, H₂C=CH, i-C₃H₇, 2-C₂H₅CH(CH₃)-
C₆H₄, Cl₃CCH₂, C₅H₁₁, c-C₁₂H₂₃, 4-t-C₄H₉-C₆H₄, C₆H₁₃, C₃H₇, CH₃OCH₂CH₂,
5 C₆H₁₃CH(CH₃), CH₃OC(CH₃)₂CH₂CH₂, C₃H₇OCH₂CH₂, CH₃OCH₂CH(CH₃), 2-i-
C₃H₇-5-CH₃-c-C₆H₉, C₄H₉OCH₂CH₂, t-C₄H₉, (CH₃)₃CCH₂, wherein

i = iso, t = tertiary, Z = cis, and c = cyclic. More preferred are bis(4-tert-
butylcyclohexyl) peroxydicarbonate, dicetyl peroxydicarbonate, and dimyristyl
peroxydicarbonate, which peroxides are solid at room temperature, and
10 diisopropylperoxydicarbonate, di-n-butylperoxydicarbonate and bis(2-
ethylhexyl)peroxydicarbonate, which are liquid at room temperature, either
pure or as a solution in isododecane. Optionally, a combination of
peroxydicarbonates or peroxydicarbonates and other peroxides may be
employed in order to influence the melt flow index of the (co)polymer and/or
15 enhance the degree of modification of the (co)polymer.

The quantity of peroxydicarbonate to be used will be dependent on the
desired degree of PP modification and on the PP employed. Preferably, use is
made of peroxydicarbonate concentrations in the range of 0.1 to 10 meq
20 (=milliequivalents=millimoles of peroxide) per 100 g PP, more preferably in the
range of 0.25 to 5 meq/100 g PP.

In another embodiment of the present invention, the modification process is
carried out in the presence of a coagent in order to influence the melt flow
25 index of the (co)polymer and/or enhance the degree of modification of the
(co)polymer.

A coagent is generally understood to be a polyfunctional reactive additive
such as a polyunsaturated compound which will react rapidly with polymer
30 radicals, will overcome steric hindrance effects and minimize undesirable side
reactions. Further information about coagents is set forth in Rubber Chemistry

and Technology, Vol. 61, pp. 238-254 and W. Hofmann, Progress in Rubber and Plastics Technology, Vol. 1, No. 2, March 1985, pp. 18-50. The term "coagent" has the same meaning as given in these publications.

5 A wide variety of useful coagents are commercially available including di- and triallyl compounds, di- and tri(meth)acrylate compounds, bismaleimide compounds, divinyl benzene, 1,3-diisopropenylbenzene and its oligomer, vinyl toluene, vinyl pyridine, parachinone dioxime, 1,2-cis-polybutadiene and their derivatives. Particularly preferred coagents include triallyl cyanurate, triallyl isocyanurate, ethylene glycol dimethacrylate and trimethylolpropane trimethacrylate.

The incorporation of an effective amount of one or more of these coagents into the (co)polymer, prior to or during the reaction with the present tend to influence the melt flow index and molecular weight of the modified (co)polymer.

Although the process of the present invention can be carried out as a batch internal mixer (Banbury) process, preferably it is performed as a continuous process.

The PP obtained using the process according to the present invention may be processed into an end product without any further adaptations if so desired. The modified PP can be processed into the desired end product in all kinds of ways known to the skilled person, with the processing conditions generally being dependent on the material and equipment employed.

Optionally, the modified PP may be purified, modified or moulded, in one or more process steps, prior to its final processing. Thus, there may be further
30 modification using another polymer or monomer in order to enhance the end product's compatibility with other materials.

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Alternatively, the modified PP may be degraded or, on the contrary, crosslinked slightly, to increase its processability and/or applicability.

- 5 Generally, to achieve the desired end conventional adjuvants, in an amount known to one skilled in the art, such as antioxidants, UV-stabilizers, lubricants, antidegradants, foaming agents, nucleating agents, fillers, pigments and/or antistatic agents are added to the PP. These adjuvants can be added to the PP before as well as during or after the modifying step
- 10 according to the invention. For example, a blowing agent can be added or gas can be injected into the extruder before, during or after the modification, in order to produce foamed PP. Preferably, a stabilizer, e.g., one or more antioxidants, is added in order to render harmless any free radicals still present in the obtained PP as well as any radicals which may be formed later
- 15 from unreacted peroxide and/or subsequent processing under air/oxygen. In a typical experiment from 0.01 to 1.0 parts per hundred parts of PP of an antioxidant are used.

- The PP obtained by the invention process does not show a substantial
- 20 difference in weight average molecular weight. Only peroxydicarbonates have been found to give the desired enhanced melt strength in the process of the present invention. Diacyl peroxides and peresters did not give such improvement in PP melt strength. While not wishing to be bound by any particular it is believed that the improvement in melt strength is caused by
- 25 modification of the PP due to the formation of alkylcarbonate-polymer adducts, with the alkylcarbonate groups originating from the peroxydicarbonate used.

- The PP obtained by the process according to the present invention may be
- 30 further processed, for example, by foaming, foam moulding, extrusion, injection moulding, blow moulding, extrusion coating, profile extrusion, or

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thermoforming. The modification reaction with peroxide may also be performed during such processing.

The invention is illustrated by the following examples.

5

Experimental

The following materials and methods are employed in the examples:

10 Polypropylene :

Hostalen® PPN 1042

copolymer of polypropylene (granules), ex Hoechst

Novolen® 3200HX

random polypropylene (granules), ex BASF

Peroxides:

15 Trigonox® EHP-C75

solution of 75% bis(2-ethylhexyl)peroxydicarbonate in isododecane, ex Akzo Nobel

Trigonox NBP-C50

solution of 50% dibutyl peroxydicarbonate in isododecane, ex Akzo Nobel

Perkadox® 16

bis(4-tert-butylcyclohexyl) peroxydicarbonate (pure), ex Akzo Nobel

20

Perkadox 26

dimyristyl peroxydicarbonate (pure), ex Akzo Nobel

Liladox® 90 P

dicetyl peroxydicarbonate (90%), ex Akzo Nobel

Miscellaneous:

25 Perkalink® 300

triallyl cyanurate (coagent), ex Akzo Nobel

Irganox® 1010

antioxidant, ex Ciba Geigy

PROCEDURE A

Mixing procedure:

30 The proper amount of the peroxydicarbonate and the antioxidant were added to 300 g of polypropylene powder in a 3 liter bucket and tumble-mixed by

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hand for 5 minutes at room temperature. Compounds were extruded immediately after mixing.

Compounding procedure:

- 5 All compounds were melt-modified by extrusion in a Haake "TW100" twin screw extruder with intensive mixing screws attached to a Haake "Rheocord System 40". During the experiment nitrogen was passed in counterflow from the hopper up through the feeder.
- 10 The extruder comprised a barrel housing four consecutive temperature chambers, wherein the first chamber had a temperature of 170°C the second 180°C, the third 180°C and the fourth chamber 190°C.
The screw speed was 50 rpm.
The extruded strand was fed through a water bath and granulated with an
- 15 Automatic "ASG5" granulator.

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PROCEDURE B

Modification procedure

Modification experiments were carried out in a Buchi 150 ml RVS laboratory autoclave ('special', type BEP280).

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The initiator was diluted to 33% with isododecane and Primol® 352. The autoclave was filled with 50 grams of polymer/anti-oxidant mixture and after closing, flushed with nitrogen (3 bar) followed by vacuum sucking (3 times) to avoid the presence of oxygen.

10

Then, the autoclave was heated up (continuous nitrogen flow, anchor stirrer speed: 150 rpm). At a polymer temperature of 155°C (measured by means of a PT100 thermocouple, directly into the polymer), the proper amount of peroxide/solvent was injected into the autoclave. The autoclave was further heated up to 230°C during 5 minutes. The reaction mixture was molten after approximately 15 minutes (total experimental time) as measured by torque increase. Then the reaction mixture was removed, cooled and granulated.

15

PROCEDURE C

20 The proper amount of the peroxydicarbonate and the antioxidant were added to polypropylene homopolymer powder and tumble-mixed at room temperature. This mixture was blended with the PP homopolymer powder and dosed to the extruder or dosed separately together with the PP copolymer granules.

25

All compounds were melt-modified by extrusion in a Werner & Pfleiderer ZSK 30 twin screw extruder.

30

The extruder comprised of a barrel housing with four consecutive temperature chambers, wherein the first chamber had a temperature of 100°C, the second and third 180°C and the fourth chamber 190°C.

The compounds were fed into the first chamber of the extruder. During the experiment nitrogen was passed in counterflow from the hopper up through the feeder. The screw speed was 200 rpm.

- 5 The extruded strand was fed through a water bath and granulated with an "Automatic ASG5" granulator.

Test procedures:

- 10 MFI (Melt Flow Index), characterizing the flow behaviour of a PP melt, was measured with a Göttfert Melt Indexer (model MP-D) according to DIN 53735 and ASTM 1238 (230°C, 21.6 N load).

- 15 Die swell, i.e. the degree to which the extrudate swells in a direction perpendicular to the direction of extrusion after it leaves the die, due to the elasticity of the PP melt, was determined by measuring the thickness of the strand coming out of the Melt Indexer and subtracting the nozzle diameter (2.1 mm) and is the mean value of ten measurements in mm. In the evaluation of the modified polypropylene the die swell was usually found to be proportional to the melt strength.

- 20 Melt strength, i.e. the ability of a melt of PP to withstand a tensile elongation or stretching without breaking, was measured using a Göttfert Rheotens attached to a Göttfert Rheograph 2001 capillary rheometer (190°C, speed 0.5 mm/s, acceleration 24 mm/s², strand length 70 mm).

- 25 In Tables 1 and 2, data on Comparative Examples A-G, preparation of PP without using a peroxydicarbonate, and Examples 1-17 according to the process of the present invention are presented (comparative examples C and D are controls with solvent without peroxide). The amounts of peroxide used
30 are expressed as milliequivalents (mmol peroxide groups) of peroxide per hundred gram of PP (meq/100 g PP).

The examples show an increased die swell and melt strength as compared with PP prepared without using a peroxydicarbonate.

- 5 The increased die swell is always related to the improvement of the elastic viscosity and melt strength.

In Table 2 data on homo-PP, co-PP and random-PP examples are shown as obtained following procedure C (examples 15 - 17, Comparative Examples F -

10 G)

In procedure C, where a Werner & Pfleiderer ZSK 30 twin screw extruder is used, a PP extrusion process on production scale was simulated where within 30 seconds residence time the compounds are melt-modified. During the
15 extrusion process the temperature of the compound increases from approximately 20°C (hopper) to approximately 190°C at the end of the extruder. In this process the peroxydicarbonate decomposes according to the Arrhenius equation dependent on the temperature and residence times in the different temperature chambers of the extruder.

20

Arrhenius equation : $K_d = A \cdot e^{-E_a/RT}$

where K_d = the rate constant for the dissociation in s^{-1}

A = the Arrhenius frequency factor in s^{-1} (for Liladox 90P: $3.02E+15$)

25 E_a = the activation energy for the peroxydicarbonate in J/mole (for Liladox 90P: $124.3E+3$)

R = 8.3142 J/mole.K

T = the temperature in K

- 30 The concentration of the initiator at any time can be calculated from the equation:

$$[I] = [I_0] \cdot e^{-K_d \cdot t}$$

where $[I_0]$ = the original initiator concentration

5 $[I]$ = the initiator concentration at time t

t = the time in seconds

Table 3 shows the amount of reacted peroxydicarbonate as a function of the temperature and residence time in the extruder as calculated by using the above equations. The compound temperature is taken as the mean temperature of the barrel temperature and a linear temperature profile (20°C to 190°C in 30 seconds).

In this procedure more than 80 %w/w of the peroxydicarbonate reacts with the PP above 120°C. Therefore the enhancement of the melt strength of PP, as a result of the reaction of peroxydicarbonate with PP, in an extrusion process mainly takes place above 120°C.

The invention is not limited to the above description, the requested rights are
20 rather determined by the following claims.

PROCEDURE A

		PROCEDURE A													
Examples		A	B	1	2	3	4	5	6	7	8	9	10	11	12
PP Borealis HC00A1-B1	Phr	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Trigonox EHP-C75	Phr			0.46	0.92					0.94					
Trigonox NBP-C75	Phr														
Perkadox 16	Phr					0.16	0.63	1.26	3.14		0.42		0.63	1.26	0.63
Liladox 90P	Phr											0.54			
Perkadox 26	Phr												0.63	1.26	0.63
Perkalink 300	Phr												0.1	0.1	0.1
Irganox 1010	Phr		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Meq. Peroxide	meq			1	2	0.25	1	2	5	2	1	1	1	2	1
peroxide / 100 g PP	/ 100 g PP														
Rheological properties															
MFI	g/10 min	2.6	2.1	1.6	1.2	1.8	1.2	0.9	0.7	1.0	1.7	1.8	1.4	1.0	1.2
Die swell	Mm	2.5	2.8	3.8	4.8	3.7	4.5	4.4	4.5	4.5	4.2	4.5	4.2	4.7	4.3
Melt strength	CN	19	23	33	33	25	38	39	40	36	35	33	36	35	36

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Table 2. Comparative Examples C - G and examples 13 - 17

Examples		PROCEDURE B							PROCEDURE C			
		C	D	13	14	15	F	G	16	17		
Homo-PP	Borealis HC00A 1-B1	phr	100	100	100	100	100	9.5	9.5	9.5	9.5	
Co-PP	Hostalen PPN 1042	phr						90.5		90.5		
Random-PP	Novolen 3200HX	phr						90.5		90.5	90.5	
Liladox 90 P Tx EHP (33 % in isodod) Tx EHP (33 % in primol) Isododecane Primol 352 Irganox 1010		phr		1.05			1.26			1.26	1.26	
		phr	0.7									
		phr	0.1	0.7 0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
		phr			2	2	2			2	2	
Meq. Peroxide	Meq peroxide / 100 g PP											
Rheological properties MFI												
Die swell	g/10 min	2.7	2.6	2.2	2.4	1.3	2.0	1.5	2.2	1.7		
Melt strength	Mm	2.9	2.8	3.4	3.2	4.4	2.4	2.3	3.6	3.5		
	CN	26	26	30	29	31						

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Table 3. Reacted peroxydicarbonate as a function of the temperature and residence time in the extruder

Residence time seconds	Barrel temperature profile °C	Linear temperature profile °C	Mean temperature profile °C	Peroxydicarbonate reacted %w/w
0	100	20	20*	0
5	180	48	114	9
7	180	62	121	20
10	180	77	128	51
15	180	105	142	93
20	180	133	156	100
30	190	190	190	100

* temperature compound in hopper (time = 0)

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CLAIMS

- 5 1. Process for enhancing the melt strength of polypropylene comprising the steps of:
 - mixing the polypropylene with at least one peroxydicarbonate;
 - reacting said polypropylene and peroxydicarbonate at a
- 10 peroxydicarbonate is not in the form of an aqueous dispersion in a polar medium with at least 90% by weight of the initiator particles being smaller than 50µm and at least 99% by weight of the initiator particles being smaller than 65µm.
- 15 2. Process according to claim 1, wherein the peroxydicarbonate is reacted with molten polypropylene.
3. Process according to claim 1 or 2, wherein the process is conducted in an extruder.
- 20 4. Process according to claim 2, wherein the temperature is from 160 to 250°C.
5. Process according to claim 4, wherein the temperature is from 170 to
- 25 225°C.
6. Process according to any of the preceding claims, wherein the peroxide comprises a peroxydicarbonate.
- 30 7. Process according to any of the previous claims, wherein the peroxydicarbonate has the formula $R^1-OC(O)OOC(O)O-R^2$, wherein R^1 and R^2 are independently selected from the group consisting of CH_3 , 2-i- $C_3H_7O-C_6H_4$, $C_2H_5CH(CH_3)$, 4- $CH_3-C_6H_4$, $Cl_3CC(CH_3)_2$, C_7H_{15} , c- $C_6H_{11}CH_2$,

- 3-t-C₄H₉-C₆H₅, Cl₃Si(CH₂)₃, C₆H₅, CH₃CH(OCH₃)CH₂CH₂, C₆H₅OCH₂CH₂,
C₆H₅CH₂, Z-C₈H₁₇CH=CH(CH₂)₈, 2-CH₃-C₆H₄, (CH₃)₂CHCH₂CH(CH₃), 3,4-
di-CH₃-C₆H₃, Cl₃C, CHCH(Cl), ClCH₂, [C₂H₅OC(O)]₂CH(CH₃), 3,5-di-CH₃-
C₆H₃, C₈H₁₇, C₂H₅, C₁₈H₃₇, 2-oxo-1,3-dioxolan-4-CH₂, C₂H₅CH(Cl)CH₂, 4-
5 CH₃O-C₆H₄, i-C₄H₉, CH₃SO₂CH₂CH₂, C₁₂H₂₅, C₆H₅CH(Cl)CH₂,
H₂C=CHC(O)OCH₂CH₂, 4-NO₂-C₆H₄, C₄H₉, C₁₀H₂₁, C₄H₉CH(C₂H₅)CH₂,
H₂C=CHCH₂, 2-Cl-c-C₆H₁₀, H₂C=C(CH₃)CH₂, c-C₆H₁₁, ClCH₂CH₂, 4-[C₆H₅-
N=N]-C₆H₄CH₂, C₁₆H₃₃, 1-naphtyl, 4-t-C₄H₉-C₆H₁₀, 2,4,5-tri-Cl-C₆H₂,
Cl(CH₂)₃, C₁₄H₂₉, 9-fluorenyl, 4-NO₂-C₆H₄CH₂, 2-i-C₃H₇-C₆H₄,
10 CH₃OCH₂CH₂, H₂C=C(CH₃), 3-CH₃-C₆H₄, BrCH₂CH₂, 3-CH₃-5-i-C₃H₇-
C₆H₃, Br₃CCH₂, C₂H₅OCH₂CH₂, 4-CH₃OC(O)-C₆H₄, H₂C=CH, i-C₃H₇, 2-
C₂H₅CH(CH₃)-C₆H₄, Cl₃CCH₂, C₅H₁₁, c-C₁₂H₂₃, 4-t-C₄H₉-C₆H₄, C₆H₁₃, C₃H₇,
CH₃OCH₂CH₂, C₆H₁₃CH(CH₃), CH₃OC(CH₃)₂CH₂CH₂, C₃H₇OCH₂CH₂,
CH₃OCH₂CH(CH₃), 2-i-C₃H₇-5-CH₃-c-C₆H₉, C₄H₉OCH₂CH₂, t-C₄H₉,
15 (CH₃)₃CCH₂, wherein
i = iso, t = tertiary, Z = cis, and c = cyclic.

8. Process according to claim 7, wherein R1 and R2 are independently
selected from the group consisting of CH₃, C₆H₅OCH₂CH₂, 4-t-C₄H₉-
20 C₆H₁₀, C₁₆H₃₃, (CH₃)₃CH₂CH(CH₃)CH₂CH₂, C₁₃H₃₇, C₄H₉, c-C₆H₁₁,
CH₃CH(OCH₃)CH₂CH₂, C₃H₇, i-C₃H₇/C₂H₅CH(CH₃), C₁₀H₂₁, C₂H₅, C₁₄H₂₉,
C₂H₅CH(CH₃), C₆H₅CH₂, C₁₈H₃₇ and C₄H₉CH(C₂H₅)CH₂.
9. Process according to claim 8, wherein the peroxydicarbonate is selected
25 from the group consisting of bis(4-tert-butylcyclohexyl) peroxy-
dicarbonate, dicetyl peroxydicarbonate, and dimyristyl
peroxydicarbonate, diisopropyl peroxydicarbonate, di-n-butylperoxy-
dicarbonate, di-sec-butylperoxydicarbonate, bis(2-
ethylhexyl)peroxydicarbonate.
- 30 10. Process according to any of the claims 7-9, wherein the
peroxydicarbonate is a liquid or preferably a solid at room temperature.

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11. Process according to claim 10, wherein the liquid is a solution of the peroxydicarbonate in an inert solvent, and is preferably bis(2-ethylhexyl)peroxydicarbonate or dibutyl peroxydicarbonate in isododecane.
- 5
12. Process according to any one of the preceding claims wherein at least one coagent is present in the reaction mixture when the polypropylene is reacted with the peroxydicarbonate.
- 10
13. Polypropylene having an enhanced melt strength obtainable using the process according to any one of the preceding claims.
14. Process for producing an extruded, melt spun or blown, moulded, thermoformed or foamed material based on a polypropylene, wherein use is made of polypropylene according to claim 13.
- 15

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 98/07219

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/00 C08K5/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 43 40 194 A (CHISSO CORP) 1 June 1994 cited in the application see page 7, line 25 - page 9, line 14 ---	1-14
Y	DE 43 21 529 A (DANUBIA PETROCHEM DEUTSCHLAND) 12 January 1995 see page 2, line 46 - line 55 ---	1-14
T	WO 97 49759 A (HOGT ANDREAS HERMAN ; AKZO NOBEL NV (NL); BOEN HO O (NL); WESTMIJZE) 31 December 1997 see page 3, line 11 - page 10, line 22 -----	1-14

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4340194 A	01-06-1994	JP 2814337 B	22-10-1998
		JP 6263823 A	20-09-1994
		JP 2844290 B	06-01-1999
		JP 6299013 A	25-10-1994
		JP 6157666 A	07-06-1994
		US 5416169 A	16-05-1995
DE 4321529 A	12-01-1995	NONE	
WO 9749759 A	31-12-1997	AU 3258497 A	14-01-1998